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## Metal–organic framework-derived $\text{CeO}_2\text{--ZnO}$ catalysts for $\text{C}_3\text{H}_6\text{-SCR}$ of NO: an *in situ* DRIFTS study

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Metal–organic framework (MOF)-based derivatives have attracted an increasing interest in various research fields. Here, we synthesized  $\text{CeO}_2\text{--ZnO}$  catalysts through the complete thermal decomposition of the Ce/MOF-5 precursor. The catalysts were characterized using XRD, FTIR, TG-DSC, SEM and  $\text{H}_2\text{-TPR}$ . It is found that the as-prepared  $\text{CeO}_2\text{--ZnO}$  is favorable for strengthening the interaction between  $\text{Ce}^{4+}$  and  $\text{Zn}^{2+}$ . A significant improvement in the catalytic performance for  $\text{C}_3\text{H}_6\text{-SCR}$  of NO was found over the Ce-doped catalysts with the highest  $\text{N}_2$  yield of 69.1% achieved over 5%  $\text{CeO}_2\text{--ZnO}$ . *In situ* DRIFTS and NO-TPD experiments demonstrated the formation of monodentate nitrates, bidentate nitrates, chelating nitrite, nitro compounds, nitrosyl and  $\text{C}_x\text{H}_y\text{O}_z$  species (enolic species and acetate) on the surface, followed by the formation of hydrocarbonate or carbonate as intermediates to directly generate  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### 1. Introduction

It is particularly notorious that the sheer quantity of gasoline and diesel powered vehicles grows with each passing day. The nitrogen oxides ( $\text{NO}_x$ ) from automobile exhaust gases have aroused significant concern among the public and government officials because these gases can cause a great threat to the environment and public health, including the greenhouse effect, acidification, photochemical smog, and ozone depletion.<sup>1,2</sup> Owing to the ground-breaking work of Iwamoto *et al.*, hydrocarbon-selective catalytic reduction (HC-SCR) has become a promising technology for clearing  $\text{NO}_x$  away from the automobile exhausts, taking into account the cost and gas components, as well as the hydrocarbons coexisting with NO in the exhaust streams.<sup>3,4</sup> Different kinds of hydrocarbons have been employed to improve the performance of HC-SCR, including propene,<sup>5</sup> methane,<sup>6</sup> ethanol,<sup>7</sup> ethylene,<sup>8</sup> and propane.<sup>9</sup> More importantly, catalysts are the core of this catalytic technology. Thus, huge efforts are dedicated to develop catalysts by both the academic community and catalyst manufacturers.

Metal–organic frameworks (MOFs) are a kind of crystalline porous materials with a periodic network structure formed by the self-assembly of inorganic metals (metal ions or clusters) and bridged organic ligands.<sup>10–14</sup> On account of their low-density structures, tunable cavities, high surface area, tailor-made chemistry and facile synthesis,<sup>10,11</sup> MOFs are good candidates for applications in gas separation and storage, as well as

catalysis.<sup>12–14</sup> Recently, researchers gradually shifted their focus from MOFs to MOF derivatives.<sup>15,16</sup> During the calcination process, MOFs are completely decomposed and gradually converted to metal oxides from the outer to inner part. Small cavities and open channels within the MOF-derived metal oxides provide pathways for the reactant species to diffuse in and out, thus enabling these metal oxides to be suitable candidates for catalysts or catalyst supports. By way of illustration, Ce-MOF was used to prepare the  $\text{CeO}_2$  catalyst for toluene combustion,<sup>16</sup> and Cu-based MOFs were applied as the precursors to attain carbon-based catalysts for low-temperature  $\text{DeNO}_x$ .<sup>15</sup> Therefore, the development of efficient functional MOF-derived metal oxides for further exploration of their practical applications has great significance.<sup>17</sup> More importantly, the composite materials usually exhibit excellent performances for environmental catalytic reactions. For example, Yang *et al.* prepared different functional composites and studied their outstanding performance of catalytic oxidative desulfurization and atrazine degradation.<sup>18,19</sup>

Cerium oxide is an extensively used promoter or catalyst support for the SCR reaction due to its superior oxygen storage capability and excellent redox properties.<sup>15</sup> The oxygen vacancies are produced during the electron transfer between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ . The reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  and enhanced oxygen transfer could facilitate the oxidation process of NO to  $\text{NO}_2$ , leading to excellent HC-SCR performance.<sup>20</sup> In addition, it can not only highly disperse the metals but also strengthen the thermal stability in reaction with other metal oxides.<sup>21</sup>

In the present study, we synthesized  $\text{ZnO}$  and  $\text{CeO}_2\text{--ZnO}$  catalysts through the complete thermal decomposition of MOF-5 and Ce/MOF-5 precursor, and then compared their activity in HC-SCR.  $\text{C}_3\text{H}_6$  was used as the reducing agent due to it being

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the major hydrocarbon component during the process of automobile exhaust emissions. First, the crystal structure, morphology and textural properties of the samples were investigated *via* XRD, TG-DSC, SEM, FTIR and H<sub>2</sub>-TPR. Second, the adsorption and activation abilities of NO were studied using temperature-programmed desorption (TPD). In addition, the *in situ* DRIFTS experiments were performed to illuminate the C<sub>3</sub>H<sub>6</sub>-SCR process as well as the possible reaction pathways.

## 2. Experimental

### 2.1. Materials

All of the reactants are of analytical grade and were used without further purification. Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,4-Benzenedicarboxylic acid (H<sub>2</sub>BDC), *N,N*-dimethylformamide (DMF) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were purchased from Macklin.

### 2.2. Catalyst preparation

MOF-5 was prepared by the solvothermal method according to the following procedures. First, 9.360 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 2.540 g H<sub>2</sub>BDC were dissolved in 190 ml *N,N*-dimethylformamide (DMF), and the resulting suspension was sonicated for 30 min. Second, the mixture was transferred into a 250 ml Teflon-lined stainless steel reactor. Then, the autoclave was placed into an oven at 120 °C for 24 h to obtain the white crystals. Subsequently, they were repetitively washed with *N,N*-dimethylformamide (DMF) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). Finally, the homogeneous material obtained was oven-dried at 120 °C for 12 h.

An impregnation technique was used to synthesize Ce/MOF-5. Namely, the predetermined amount of cerium nitrate (Ce(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and MOF-5 precursor were dissolved in ethyl alcohol and the mixed solution was sonicated for 30 min. Afterward, the mixture was left to equilibrate at room temperature for 24 h. Finally, the product was dried at 100 °C for 12 h, followed by calcination at 600 °C for 2 h under air to obtain the CeO<sub>2</sub>-ZnO catalysts, and were denoted as 1% CeO<sub>2</sub>-ZnO, 3% CeO<sub>2</sub>-ZnO, 5% CeO<sub>2</sub>-ZnO, and 10% CeO<sub>2</sub>-ZnO.

### 2.3. Catalysts characterization

In the present study, we adopted a series of methods to evaluate the crystal structure, morphology, thermal stability, reducibility and adsorption properties of the catalysts. XRD patterns were gained on the Empyrean (PANalytical B.V.) using Cu K $\alpha$  radiation and the X-ray tube was operated under 40 kV and 40 mA. All the as-synthesized samples were scanned over the 2 $\theta$  range between 5° and 80° at a scan speed of 10° min<sup>-1</sup>. The surface morphology of all the samples was characterized by SEM (S-4800, Japan). Thermogravimetric and differential scanning calorimetry (TG-DSC) analysis curves were obtained using a STA409pc (NETZSCH German) synchronous thermal analyzer. The samples were heated from 30 °C to 700 °C at a rate of 5 °C min<sup>-1</sup> under a flow of nitrogen at 40 ml min<sup>-1</sup>. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) and NO

temperature-programmed desorption (NO-TPD) were performed on a Chembet PULSAR TPR/TPD chemisorption analyzer loaded with 50 mg samples. Prior to the reduction, the sample was pretreated under pure He atmosphere at 350 °C for 30 min for the sake of removing the absorbent (*e.g.*, H<sub>2</sub>O). In the case of H<sub>2</sub>-TPR, the sample began from room temperature to 800 °C under an H<sub>2</sub> stream at a rate of 10 °C min<sup>-1</sup>. For NO-TPD, the sample was treated in a flow of NO at 100 °C for 60 min, followed by heating from 100 °C to 300 °C for desorption at a rate of 10 °C min<sup>-1</sup>. Fourier transform infrared spectroscopy (FT-IR) was performed on a VERTEX German infrared spectrometer with the KBr pellet technique at room temperature. Spectra were collected in the range of 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

### 2.4. Catalytic performance test

The C<sub>3</sub>H<sub>6</sub>-SCR catalytic tests were performed in a fixed-bed quartz tube reactor. Prior to an experiment, a catalyst (200 mg) was pretreated at 300 °C for 1 h in an Ar stream, and the activity measurement was carried out from 150 °C to 350 °C at a heating rate of 10 °C min<sup>-1</sup>. The reaction conditions were as follows: 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>, 5 vol% O<sub>2</sub> and Ar as balance; the total gas flow rate was 100 ml min<sup>-1</sup> and the GHSV was 30 000 h<sup>-1</sup>. The concentrations of N<sub>2</sub> in the effluent gas were analyzed on-line using a gas chromatograph. The conversion of NO to N<sub>2</sub> was calculated as follows:

$$\text{NO conversion to N}_2 = 2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}} \times 100\% \quad (1)$$

### 2.5. *In situ* DRIFTS measurements

NO and C<sub>3</sub>H<sub>6</sub> adsorption on the catalysts were recorded using a FT-IR spectrometer (VERTEX German). Concentrations of the reactants were 1000 ppm of NO, 1000 ppm of C<sub>3</sub>H<sub>6</sub>, 5 vol% oxygen. The sample (20 mg) was mounted in a quartz DRIFTS cell and activated by calcination in Ar stream (30 ml min<sup>-1</sup>) at 300 °C for 30 min before introducing the reaction mixtures, followed by cooling to the desired temperature, and then the spectrum was collected and used as the background. All spectra were recorded at a resolution of 4 cm<sup>-1</sup> (number of scans, 32) in the range of 4000–400 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Physical and texture characterizations

From the X-ray diffraction profiles, we can identify the transformation in the phase texture on the MOF-5, MOF-5-derived ZnO and CeO<sub>2</sub>-ZnO samples. Fig. 1(a) exhibits the previous diffraction peaks for MOF-5; the 2 $\theta$  angles of 6.85°, 9.62°, 13.69°, 15.39° correspond to the (200), (220), (400), (420) planes.<sup>11</sup> A sharp peak appeared at 6.85°, which proved that we successfully synthesized the MOF-5 materials with high crystallinity.<sup>11</sup> From the MOF-5-derived composite characterization, it can be observed that the primary structure of the framework collapsed and the characteristic diffraction peaks completely



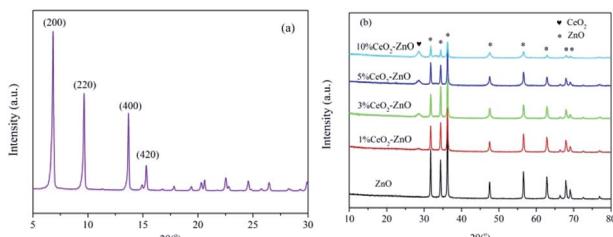


Fig. 1 XRD pattern of (a) MOF-5 and (b) ZnO and  $\text{CeO}_2$ -ZnO.

disappeared, with the main peaks of the wurtzite ZnO structure appearing at  $31.7^\circ$  (100),  $34.4^\circ$  (002),  $36.3^\circ$  (101),  $47.4^\circ$  (102),  $56.6^\circ$  (110),  $62.8^\circ$  (103),  $67.9^\circ$  (112) and  $69.1^\circ$  (201) (JCPDS No. 36-1451).<sup>22</sup> The sample with Ce loading also displays an additional XRD peak corresponding to the structure of  $\text{CeO}_2$ , indicating that the doped-Ce species exists in the form of  $\text{CeO}_2$  (Fig. 1(b)).

The thermogravimetric and differential scanning calorimetry (TG-DSC) curves of the fresh MOF-5 are shown in Fig. 2. Three noticeable weight loss events were evident. The continuous weight loss of about 4% at the temperature range between  $50^\circ\text{C}$  and  $100^\circ\text{C}$  was caused by the evaporation of water from the surface of the sample. The second major loss in the temperature range of  $150$ – $320^\circ\text{C}$  was about 27%, which was related to the evaporation and decomposition of residual organic components (DMF).<sup>23</sup> The most prominent weight loss appeared at a temperature over  $420^\circ\text{C}$ , and the weight loss rapidly reached almost 60%, demonstrating that the MOF-5 framework had collapsed. According to the previous study, for MOF-5, the breakdown of the carboxylic bridges between the benzene rings and  $\text{Zn}_4\text{O}$  clusters results in the decomposition of the organic ligand molecules to form  $\text{CO}_2$  and benzene.<sup>11</sup> The DSC curve also shows a sharp exothermic peak between  $420^\circ\text{C}$  and  $485^\circ\text{C}$  with a maximum peak temperature at  $480^\circ\text{C}$  due to the decomposition of the organic components. The decomposition process was completed after  $550^\circ\text{C}$ . The evidence from the thermogravimetric analysis verified that the MOF-5 crystal transformed into ZnO completely above  $550^\circ\text{C}$ . In view of these results, we chose  $600^\circ\text{C}$  as the calcination temperature to attain the oxides.

The FTIR spectra of the as-prepared MOF-5-derived ZnO and  $\text{CeO}_2$ -ZnO catalysts are shown in Fig. 3. A significant peak at  $430\text{ cm}^{-1}$  may be attributed to the Zn–O stretching vibrations.<sup>23</sup>

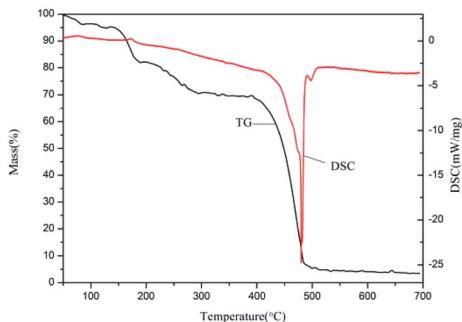


Fig. 2 TG profile for the MOF-5 precursor.

The band at  $1620\text{ cm}^{-1}$  is ascribed to the bond stretching of the carboxyl ( $\text{O}=\text{C}-\text{OH}$ ) functional groups on the surface of the samples.<sup>24</sup>

### 3.2. Morphology

Scanning electron microscopy is a technique that enables the study of the microstructure of nanoparticles. The scanning electron micrographs of MOF-5, and the MOF-5-derived ZnO and  $\text{CeO}_2$ -ZnO catalysts are presented in Fig. 4. The MOF-5 samples clearly exhibit the cubic morphology with smooth facets and the particle size ranged from  $200\text{ nm}$  to  $500\text{ nm}$  (Fig. 4(a)). After thermal treatment at  $600^\circ\text{C}$ , the MOF-5-derived ZnO and  $\text{CeO}_2$ -ZnO catalysts (Fig. 4(b) and (c)) mainly maintain the cubic structure, but the edge becomes smooth and the surface appears porous. In addition, compared to MOF-5, the particle sizes of the ZnO and  $\text{CeO}_2$ -ZnO catalysts show a slight decrease. During the heat-treatment of MOF-5 and Ce/MOF-5, as expected, they gradually decompose with time, resulting in the smaller and porous particles with cubic structure.

### 3.3. H<sub>2</sub>-TPR measurements

$\text{H}_2$ -TPR analysis was performed to determine the reducibility of the MOF-5-derived ZnO and  $\text{CeO}_2$ -ZnO catalysts. As shown in Fig. 5, one obvious hydrogen consumption peak centered at  $600^\circ\text{C}$  exists in each sample. Compared with the ZnO catalyst, the  $\text{CeO}_2$ -ZnO catalyst presented an obvious shift towards lower temperatures with the increasing amount of Ce, suggesting that the redox properties of the catalysts were enhanced by the interaction between  $\text{CeO}_2$  and ZnO. The enhanced redox properties could lead to a better dispersion, promoting oxygen mobility and the oxidation process of NO to  $\text{NO}_2$ .

### 3.4. Catalytic test

The  $\text{N}_2$  yield as a function of temperature over the MOF-5-derived ZnO and  $\text{CeO}_2$ -ZnO catalysts is shown in Fig. 6. The MOF-5-derived ZnO achieved the maximum  $\text{N}_2$  yield of 31.5% at  $250^\circ\text{C}$ , while the activity of the Ce-doped catalysts was enhanced significantly, though the temperature corresponding to the maximum  $\text{N}_2$  yield shifted to a higher temperature at  $270^\circ\text{C}$ . Among the tested catalysts, 3%  $\text{CeO}_2$ -ZnO and 5%  $\text{CeO}_2$ -ZnO exhibited outstanding catalytic performances, with a maximum  $\text{N}_2$  yield of 68.3% and 69.1%, respectively. The

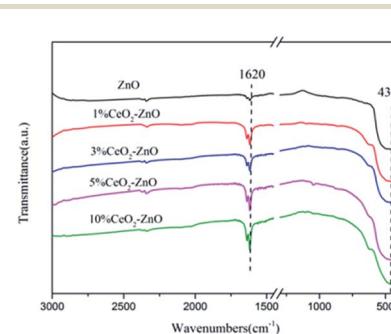
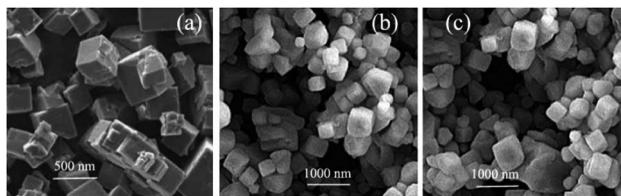
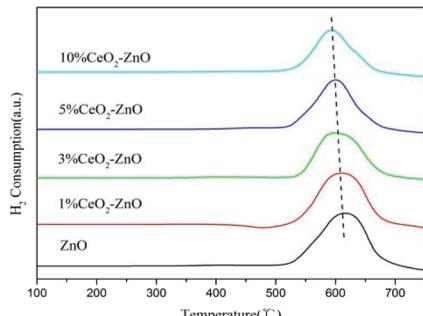
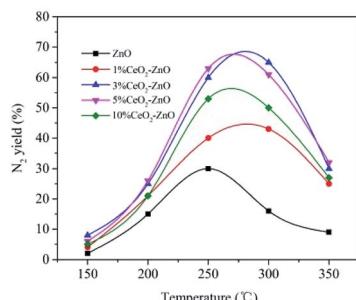


Fig. 3 FT-IR spectra of ZnO and  $\text{CeO}_2$ -ZnO catalysts.

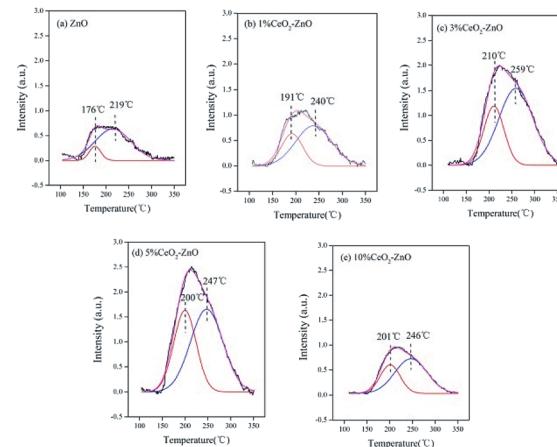


Fig. 4 SEM images of (a) MOF-5, (b) ZnO and (c)  $\text{CeO}_2$ –ZnO.Fig. 5  $\text{H}_2$ -TPR spectra of the ZnO and  $\text{CeO}_2$ –ZnO catalysts.Fig. 6  $\text{N}_2$  yield as a function of temperature for the ZnO and  $\text{CeO}_2$ –ZnO catalysts.

unsatisfactory performance of the 10%  $\text{CeO}_2$ –ZnO catalyst (55.7%) may be attributed to the agglomeration of excess Ce.

### 3.5. NO-TPD measurements

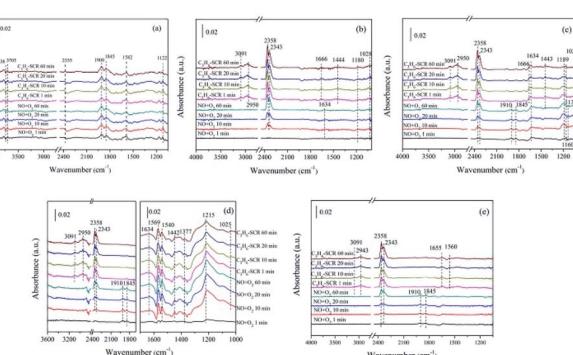
To evaluate the NO adsorption ability of the as-synthesized catalyst, NO-TPD measurements were conducted to explore the interaction between NO and the samples (Fig. 7). For the MOF-5-derived ZnO catalyst, two NO desorption peaks at 176 and 219 °C could be observed. The two peaks shifted to higher temperatures after Ce was added to the catalysts, indicating that Ce can largely strengthen the bonding of NO with the catalyst surface. Moreover, the intensities of the two NO desorption peaks enhanced after the addition, which indicated that adding Ce can result in the redistribution of the adsorbed  $\text{NO}_x$  species, thus facilitating the NO oxidation. It is worth noting that the promotion effect enhanced very slowly after Ce loading, reaching over 10%. This might be caused by agglomeration of the excess Ce.

Fig. 7 NO-TPD profiles of the ZnO and  $\text{CeO}_2$ –ZnO catalysts.

### 3.6. DRIFTS studies

**3.6.1. Adsorption of NO followed by  $\text{C}_3\text{H}_6/\text{O}_2$  over time.** In order to investigate the surface reactions and intermediates, a series of *in situ* DRIFTS experiments were performed. Fig. 8 shows the *in situ* DRIFTS spectra obtained after exposure to 1000 ppm NO and 5%  $\text{O}_2$  in Ar, followed by 1000 ppm  $\text{C}_3\text{H}_6$  and 5 vol%  $\text{O}_2$  in Ar at 250 °C. In the case of the MOF-5-derived ZnO catalyst (Fig. 8(a)), NO and  $\text{O}_2$  flushing at 250 °C produced several bands. The bands at 1122  $\text{cm}^{-1}$  and 1582  $\text{cm}^{-1}$  are attributed to the bidentate nitrates,<sup>25,26</sup> which are formed when the NO molecules bridge two adjacent oxygen atoms.<sup>25</sup> In addition, the nitrosyl (adsorbed NO) (1845  $\text{cm}^{-1}$  and 1900  $\text{cm}^{-1}$ ),<sup>27,28</sup> hydroxyl group (3705  $\text{cm}^{-1}$  and 3738  $\text{cm}^{-1}$ ),<sup>27,28</sup> and gas phase  $\text{CO}_2$  (2355  $\text{cm}^{-1}$ )<sup>29</sup> also appeared. Upon switching to  $\text{C}_3\text{H}_6$  and  $\text{O}_2$ , the surface bidentate nitrates decreased slightly with time, while the other bands remained unchanged.

In the case of the 1%  $\text{CeO}_2$ –ZnO catalyst (Fig. 8(b)), the formation of monodentate nitrate, chelating nitrite and gas-phase NO (1028  $\text{cm}^{-1}$ , 1180  $\text{cm}^{-1}$  and 1634  $\text{cm}^{-1}$ , respectively) occurred on the surface after 10 min and was slightly enhanced with increasing time. Switching to the  $\text{C}_3\text{H}_6/\text{O}_2$  mixture, several new bands were detected. The bands at

Fig. 8 *In situ* DRIFTS of (a) ZnO, (b) 1%  $\text{CeO}_2$ –ZnO, (c) 3%  $\text{CeO}_2$ –ZnO, (d) 5%  $\text{CeO}_2$ –ZnO (e) 10%  $\text{CeO}_2$ –ZnO exposed to the SCR reaction at 250 °C for various times under NO +  $\text{O}_2$  adsorption and during  $\text{C}_3\text{H}_6$  interaction with the NO +  $\text{O}_2$  gas mixture.

1666  $\text{cm}^{-1}$  and 1444  $\text{cm}^{-1}$  are assigned to the enolic species ( $\text{RCH}=\text{CH}-\text{O}^-$ ) and acetic acid, respectively.<sup>27,28</sup> The IR bands centered at 2950  $\text{cm}^{-1}$  and 3091  $\text{cm}^{-1}$  are attributed to the asymmetric and symmetric CH stretch ( $\nu\text{CH}$ ) of the  $\text{CH}_3$  group, which were proposed by Efthathiou *et al.* to indicate the  $-\text{CH}_3$  adsorbed species produced from the interaction of  $\text{C}_3\text{H}_6$  with the catalyst surface.<sup>30</sup> In addition, a large amount of gas phase  $\text{CO}_2$  was observed at 2343  $\text{cm}^{-1}$  and 2358  $\text{cm}^{-1}$ .

For the 3%  $\text{CeO}_2$ -ZnO catalyst (Fig. 8(c)),  $\text{NO}/\text{O}_2$  flushing after 1 min produced the monodentate nitrate (at 1028 and 1137  $\text{cm}^{-1}$ ), chelating nitrite (at 1160 and 1189  $\text{cm}^{-1}$ ), nitrosyl (at 1845  $\text{cm}^{-1}$  and 1910  $\text{cm}^{-1}$ ), and gas-phase NO (at 1634  $\text{cm}^{-1}$ ), indicating that the 3%  $\text{CeO}_2$ -ZnO catalyst exhibited better adsorption performance in comparison with the 1%  $\text{CeO}_2$ -ZnO catalyst. In addition, the peaks at 2343 and 2358  $\text{cm}^{-1}$  belong to the gas phase  $\text{CO}_2$  and are attributed to the  $\text{C}=\text{O}$  bonds on the carbon surface. The intensities of these peaks were markedly increased by prolonging the adsorption time. Similar to the 1%  $\text{CeO}_2$ -ZnO catalyst, the chelating nitrite and nitrosyl group clearly decreased after purging with  $\text{C}_3\text{H}_6/\text{O}_2$ , accompanied by an appearance of the enolic species (1666  $\text{cm}^{-1}$ ) and acetate (1443  $\text{cm}^{-1}$ ) over 3%  $\text{CeO}_2$ -ZnO.

In the case of the 5%  $\text{CeO}_2$ -ZnO catalyst (Fig. 8(d)), excluding the similar characteristic peaks with the 1%  $\text{CeO}_2$ -ZnO and 3%  $\text{CeO}_2$ -ZnO catalysts, several new bands such as the bidentate nitrate (1569 and 1540  $\text{cm}^{-1}$ ) and nitro compounds (1280  $\text{cm}^{-1}$ ) were observed at the same time, suggesting the enhanced adsorption ability of NO on the 5%  $\text{CeO}_2$ -ZnO catalyst. For 10%  $\text{CeO}_2$ -ZnO (Fig. 8(e)), the peaks were significantly weakened, revealing that the doping amount of cerium should be appropriate for the ceria-zinc mixed oxides.

On the basis of these facts, we can reach the following conclusion. The nitrates (monodentate nitrates, bidentate nitrates), chelating nitrite, nitro compounds and nitrosyl groups are formed on the surface of the catalysts from the interaction of NO and  $\text{O}_2$ . After introducing  $\text{C}_3\text{H}_6$ , these species decreased or diminished, accompanied by hydrocarbonate, enolic species and acetate. In addition, significant amounts of gas phase  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (the products of  $\text{C}_3\text{H}_6$  oxidation) were also observed. All of the bands were significantly enhanced by adding ceria.

**3.6.2. Adsorption of  $\text{C}_3\text{H}_6/\text{O}_2$  followed by NO at 250  $^\circ\text{C}$  on the 5%  $\text{CeO}_2$ -ZnO catalyst.** To determine the adsorption and activation of  $\text{C}_3\text{H}_6$  in the presence of  $\text{O}_2$  and to study the reactivity of the adsorbed  $\text{NO}_x$  species, a mixture of  $\text{C}_3\text{H}_6$  and  $\text{O}_2$ , followed by NO were flowed over the catalysts at 250  $^\circ\text{C}$ . The DRIFTS spectra of the ZnO catalyst were not apparent here; thus, we selected the 5%  $\text{CeO}_2$ -ZnO catalyst for the DRIFTS measurements. As observed in Fig. 9, after purging with  $\text{C}_3\text{H}_6/\text{O}_2$ , the C-H bending mode of the  $-\text{CH}_3$  group for the adsorbed hydrocarbonate could be observed by the band at 1440  $\text{cm}^{-1}$ . The -CH stretching vibrations (2953  $\text{cm}^{-1}$  and 3101  $\text{cm}^{-1}$ ) were assigned to the unsaturated hydrocarbon fragments. In addition, the bands for  $\text{C}_x\text{H}_y\text{O}_z$  (at 1636  $\text{cm}^{-1}$ ) and  $\text{C}_3\text{H}_6$  in the gas phase (at 1666  $\text{cm}^{-1}$ ) were recorded.

Exposure to NO resulted in the surface  $\text{C}_x\text{H}_y\text{O}_z$ , hydrocarbonate and  $\text{C}_3\text{H}_6$  gas fade away, combined with an

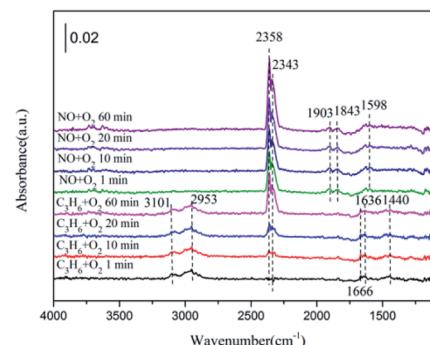


Fig. 9 *In situ* DRIFTS of 5%  $\text{CeO}_2$ -ZnO exposed to the SCR reaction at 250  $^\circ\text{C}$  for various times under  $\text{C}_3\text{H}_6 + \text{O}_2$  adsorption and during  $\text{NO} + \text{O}_2$  interaction with the  $\text{C}_3\text{H}_6 + \text{O}_2$  gas mixture.

enhancement in the bidentate nitrate (at 1598  $\text{cm}^{-1}$ ) and nitrosyl (at 1845  $\text{cm}^{-1}$  and 1910  $\text{cm}^{-1}$ ) species. More importantly, the formation of  $\text{CO}_2$  (2358 and 2343  $\text{cm}^{-1}$ ) was increased by the flow of NO. The  $\text{C}_x\text{H}_y\text{O}_z$  amounts decreased by the reaction with NO, although the hydrocarbonate species were more likely to decompose directly to  $\text{CO}_2$  and  $\text{O}_2$ .

**3.6.3. Co-adsorption of  $\text{C}_3\text{H}_6 + \text{O}_2$  with different  $\text{O}_2$  content.** It is reported that oxygenated hydrocarbon formation is crucial to the production of the  $\text{C}_x\text{H}_y\text{O}_z$  species, which are considered to be important intermediates for HC-SCR.<sup>31</sup> In order to understand the reactivity of the partially oxidized species from  $\text{C}_3\text{H}_6$  due to different  $\text{O}_2$  content, the *in situ* DRIFTS spectra of 5%  $\text{CeO}_2$ -ZnO exposed to  $\text{C}_3\text{H}_6 + \text{O}_2$  with different  $\text{O}_2$  content after 30 min are recorded. A similar changing trend was observed in Fig. 10. Spectral features from the hydrocarbon fragment (1442, 2881, 2953 and 3101  $\text{cm}^{-1}$ ), surface  $\text{C}_x\text{H}_y\text{O}_z$  (1636  $\text{cm}^{-1}$ ) and gas-phase  $\text{C}_3\text{H}_6$  (1666  $\text{cm}^{-1}$ ) emerged. With increasing the  $\text{O}_2$  content, the intensities of all the peaks significantly increased. This fact indicates that the adsorption and activation of  $\text{C}_3\text{H}_6$  could be promoted as the  $\text{O}_2$  content increased. It is worth noting that the promotion effect was enhanced very slowly as the  $\text{O}_2$  content reached 10 vol%. This result implies that the excess  $\text{O}_2$  cannot accelerate the  $\text{C}_3\text{H}_6$  activation and adsorption any more.

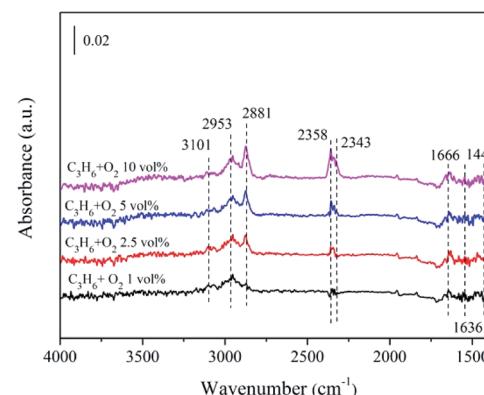


Fig. 10 *In situ* DRIFTS of 5%  $\text{CeO}_2$ -ZnO exposed to  $\text{C}_3\text{H}_6 + \text{O}_2$  with different  $\text{O}_2$  content after 30 min.

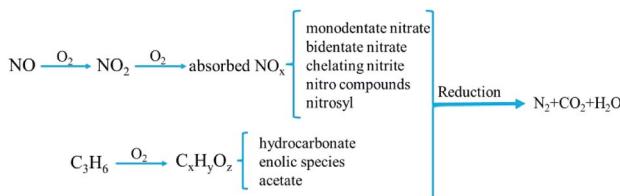


Fig. 11 Proposed reaction mechanism of  $\text{NO}_x$  reduction by propene over  $\text{CeO}_2\text{-ZnO}$  catalysts.

### 3.7. Reaction pathway

Many literature reports have confirmed that NO reduction undergoes different reaction pathways, depending on the type of hydrocarbon reductants and SCR catalysts, along with the reaction temperature.<sup>32</sup> In general, two schemes are proposed for the process. One is known as the “decomposition” mechanism, involving the dissociation and adsorption of NO on the metal active sites, followed by the recombination of the adsorbed N to generate the gas-phase  $\text{N}_2$ . The other is the “reduction” mechanism, which consists of complex surface interactions between the adsorbed  $\text{NO}_x$  and surface hydrocarbon fragments.<sup>33,34</sup>

In this study, the reaction mechanism of the HC-SCR over the MOF-5-derived  $\text{CeO}_2\text{-ZnO}$  catalysts conforms to the “reduction” mechanism scheme. It can be understood through an analysis of the adsorbed species by means of *in situ* DRIFTS. The scheme of reaction mechanism is shown in Fig. 11. First, during the adsorption and subsequent oxidation of NO process, the nitrates (monodentate nitrates, bidentate nitrates), chelating nitrite, nitro compounds and nitrosyl are generated on the active sites ( $\text{Ce}^{4+}$  and  $\text{Zn}^{2+}$ ). In addition, an abundance of  $\text{C}_x\text{H}_y\text{O}_z$  (enolic species and acetate) is formed and activated on the active sites ( $\text{Ce}^{4+}$  or  $\text{Zn}^{2+}$ ). Subsequently, in the typical  $\text{C}_3\text{H}_6$ -SCR, the two kinds of surface species above are able to react with each other through the formation of a hydrocarbonate or carbonate species, and then directly produce  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Based on our present study, these results demonstrate that the Ce addition has a significant positive effect on the formation of more adsorbed  $\text{NO}_x$  species due to the increase in the available active sites, and contributes to the improvement in the  $\text{C}_3\text{H}_6$ -SCR activity.

## 4. Conclusions

In summary, the MOF-based derivative  $x\%$   $\text{CeO}_2\text{-ZnO}$  ( $x = 1, 3, 5, 10$ ) catalysts were facilely synthesized using a complete thermal decomposition of the Ce/MOF-5 precursor. Combined with XRD, FTIR, TG-DSC, SEM and  $\text{H}_2$ -TPR experiments, it was found that the as-prepared  $\text{CeO}_2\text{-ZnO}$  catalysts were favorable for strengthening the interaction between  $\text{Ce}^{4+}$  and  $\text{Zn}^{2+}$  and exhibited excellent catalytic performance for the  $\text{C}_3\text{H}_6$ -SCR of NO. A significant improvement in the catalytic activity was found over the Ce-doped catalysts with the highest  $\text{N}_2$  yield of 69.1% achieved over 5%  $\text{CeO}_2\text{-ZnO}$ . *In situ* DRIFTS and NO-TPD experiments demonstrated the formation of monodentate

nitrates, bidentate nitrates, chelating nitrite, nitro compounds, nitrosyl and  $\text{C}_x\text{H}_y\text{O}_z$  species (enolic species and acetate) on the surface, and the additional formation of hydrocarbonate or carbonate as intermediates to directly generate  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, this research highlights new perspectives on the application of MOF materials in the field of de $\text{NO}_x$ .

## Conflicts of interest

There are no conflicts to declare.

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